Accelerated Tests for the Settling of Pigments in Paints

New Jersey zinc

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Accelerated Tests for the Settling of Pigments in Paints

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The New Jersey Zinc Company is glad to make this contribution as a part of its work in the interests of the paint industry.

Foreword

SHELF storage of products has always been one of the paint manufacturer's problems. Although there is a considerable quantity of informative data available on this subject, no satisfactory method for determining the settling tendencies of paints has been offered.

Most of the published data are the results of observations of natural settling over extended periods of time. This procedure, however, is a discouraging undertaking because of the slow progress and delayed results.

In other cases, attempts have been made to accelerate the settling by various methods, such as decreasing the pigment-vehicle ratio by the addition of vehicle, decreasing the viscosity of the vehicle with extra volatile thinner or increasing the effective specific gravity of the pigment mixture by eliminating a light constituent. Also, settling tests have been suggested which are based on the omission from a formula of a flocculating material or one that possessed suspending properties. But any procedure which depends on a change in the formulation of the product under examination is not entirely satisfactory or suitable for general application.

According to the premises of the following paper, settling is primarily due to differences in gravitational forces on the various constituents. The rate of saponification and the hardening or caking of the settled pigment, which is an important phase of settling difficulties, is affected primarily by heat.

With these facts in mind, an accelerated settling test has been developed which involves a combination of centrifuging and heating. The samples are kept in small glass jars so that the amount of settled pigment and the supernatant liquid can be measured and any gel or skin easily observed. These jars are placed in a temperature cabinet where they are kept at 65° to 70° C all of the time except the twenty minutes in the morning and evening when they are centrifuged at 1000 r.p.m.

This acceleration routine was developed on flat wall paints because, with the possible exception of certain specialties, these paints as a rule offer more settling difficulties than other types. This method should be applicable, however, with suitable modifications to any paint, enamel, or lacquer. In flat wall paints, the effects of long periods of natural aging have been obtained in four or five days by application of this accelerating routine.

The results of the accelerated tests have been compared with those obtained through natural aging.

To further check the effectiveness of these accelerated tests, commercial paints of known settling tendencies were subjected to the above routine for seven days. This test was found to be equivalent to more than two years normal aging and the accelerated results agreed with those obtained under normal conditions.

After the samples have been subjected to this routine the condition of the settled mass is determined by a penetrometer, the unit of measure being the weight required to produce complete penetration by standard plungers within thirty seconds.

A method for determining the work required to reincorporate the settled pigment is also included. The stirring apparatus described has successfully broken up and reincorporated the hardest types of caked pigment. The time of stirring required to produce a smooth paint mixture is an indication of the hardness of the settled mass. This is considered a valuable addition to the settling test inasmuch as it is of commercial importance that a settled paint reincorporate readily.

It is possible to study the causes of the settling through microscopic examination of the caked pigment. This phase of the investigation is still under way.

* * *

Since the first presentation of this paper the method described has been used extensively for determining the settling tendencies of various types of flat wall paints. Although the settling produced by the test is generally typical of that which occurs when the paint is stored under normal conditions, for an occasional paint the accelerated results may be decidedly misleading. Discrepancies between the accelerated and natural settling usually occurs with flat wall paints possessing false bodies, induced by artificial bodying agents. This type of paint maintains its false body if not agitated, but readily breaks down when stirred. If not disturbed, the pigment in such a paint may remain in suspension almost indefinitely, but if occasionally moved, jarred, or shaken, objectionable settling often occurs. The test described in this paper produces results more comparable to natural storage in which occasional movement or handling of the paint occurs.

Accelerated Tests for the Settling of Pigments in Paints

By Sidney Werthan and R. H. Wien

Research Division, The New Jersey Zinc Company[1]

ANY test by which the settling tendencies of a paint can be determined before it is packed and distributed should be of value to the manufacturer. In this paper the various factors effecting the settling rate or tendency are briefly considered, accelerated tests based on these factors are described and methods for examining the degree and nature of the settled cake are given. Although the settling of pigment in barrels, drums, dipping tanks and the containers used with spraying and other paint application equipment often causes difficulty, this paper is limited to the discussion of settling in small size packages or so-called "Shelf Goods."

In the development of an accelerated settling test, one must first consider the factors involved and the variations in these that promote settling tendencies. These factors are the properties of the pigment and of the vehicle, pigment-vehicle ratio, type of container and storage conditions.

Some of the properties of the pigment that influence settling tendencies are the size of the particles or the relative particle sizes of the various components of the pigment mass, the density or relative densities, and the activity which includes such properties as basicity, wettability, soap forming, flocculating, dispersing and gel forming tendencies. Those properties of the vehicle, variations in which influence settling tendencies, are specific gravity, viscosity, volatile-non-volatile ratio, and activity, which includes acidity, stability, wetting, dispersing and flocculating properties.

Changing the pigment-vehicle ratio, that is, increasing the vehicle content is one of the simplest means of promoting settling. Although the type of container does not influence settling, the use of tall cylindrical jars magnifies the relative differences between samples. Both rate of settling and subsequent caking, increase with heat. As settling is primarily due to the differences in the gravitational forces on the various constituents of the paint, any increase in this force will hasten settling.

[1]Revision of a paper presented before the Division of Paint and Varnish Chemistry at the 75th Meeting of the American Chemical Society, St. Louis, Mo., April 16 to 19, 1928.

Series of Flat Wall Paints containing additional Mineral Spirits

Mixture of Pigment and Vehicle Prepared Paint

Comparison Between Rapid Test in which Pigment and Vehicle are just Mixed and Test Using Prepared Paints

Based on these different factors, various tests have been developed. The rate of settling in a paint can often be accelerated by eliminating one of the pigment constituents, as, for example, a coarse, fibrous pigment or one of low specific gravity (such as fibrous talc) or one that has suspending properties due to soap forming tendencies (such as zinc oxide) or one that reacts with the vehicle to form a gel (such as aluminum stearate). Tests of this kind are usually quite limited in their application and should be adopted only after careful preliminary experimentation has proven that the change in the pigment formula has only resulted in accelerating the normal settling of the balance of the pigment constituents.

Perhaps the simplest means of testing a specific formula is to alter the vehicle or the pigment-vehicle ratio by adding extra thinner. The addition of thinner has a threefold effect; it increases the vehicle content, decreases the specific gravity of the vehicle and decreases its viscosity. Decreasing the pigment-vehicle ratio of a series of flat wall paints from 71-29 to 60-40 by the addition of mineral spirits made it possible to obtain settling indications within ten days that were fairly representative of the settling in the regular products after six months' storage.

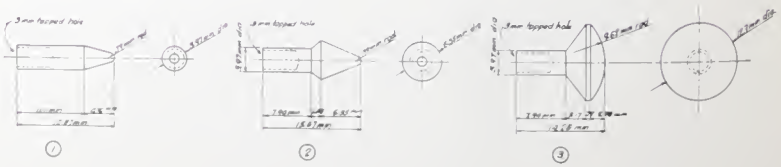
A very simple application of this type of test is to just mix, by shaking (without any milling) the pigment with the reduced vehicle. Sometimes the results so obtained are misleading, so it is preferable to add extra thinner to the regular paints. Still, with certain formulae, the same relative results were obtained whether extra thinner was added to the paint or the pigment merely mixed with the reduced vehicle. The results were also comparable with the settling in the regular paints after prolonged storage.

Rate of settling may be increased by eliminating a flocculating constituent, such as an emulsifying agent from the vehicle. Also increasing the dispersing properties of the vehicle by the addition of a small percentage of polymerized oil or a thinner possessing high solvent powers has a similar effect. As in previous methods discussed, any test based on increasing the dispersing properties of the vehicle necessitates preliminary investigation to establish the value of the results obtained.

A test suitable for general application should not necessitate altering the product under examination. Objectionable settling is the combined result of migration of the pigment toward the bottom of the container and reactions within the paint. The centrifuge offers the simplest means of increasing the rate of migration of the pigment and heat is the most logical agent for accelerating the activities that produce caking. The rate of migration can be controlled by regulating the speed of the centrifuge, while, by a careful selection of temperature, the maximum ac-

PENETROMETER

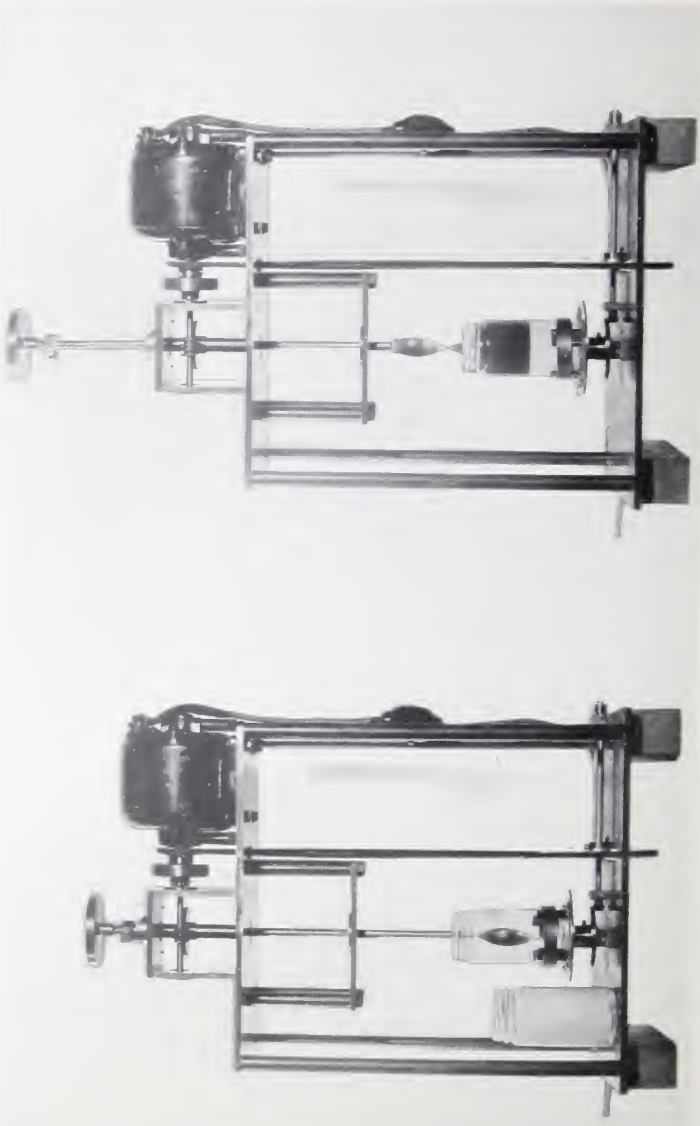
PENETROMETER PLUNGERS



celeration of normal aging can be produced. The most promising accelerated test consists of a combination of centrifugal force and heat and the perfect test depends on obtaining the correct balance. The ideal condition would be to apply the correct centrifugal speed, under the proper temperature, which would necessitate a controlled temperature room or cabinet for the centrifuge. Satisfactory results can be obtained by intermittently centrifuging the warm sample. It is necessary to determine a suitable cycle, care being taken that a temperature is not used that is sufficiently high to cause reactions in the paint which normally would not occur. The cycle chosen will generally depend on the equipment available and the degree of acceleration desired.

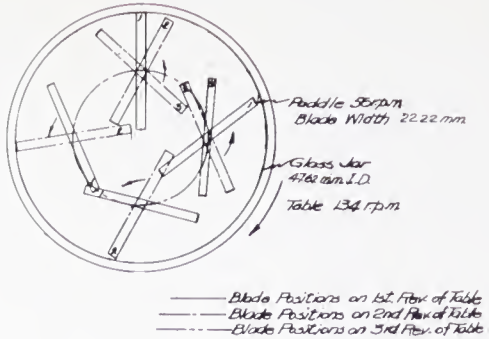
This laboratory uses a twenty-four hour cycle, which is quite severe as only four to five days are required to reproduce conditions typical of two years' normal storage. Tests are made in small glass jars with metal covers. These jars are approximately six centimeters in diameter and eleven centimeters tall with a capacity of 180 c.c. This jar was arbitrarily chosen because of the size of the cups on the centrifuge. In the present cycle the jar of paint is kept in a warm oven (65°-70° C.) overnight (approximately eighteen hours). The following morning the warm sample is centrifuged for twenty minutes at 1000 r.p.m., returned to the oven for approximately five hours, centrifuged again for twenty minutes and, unless it is to be examined, the cycle is repeated. A sample, before being examined, is brought to room temperature. Although most of the work has been with flat wall paints, the results indicate that this test is applicable to other paints, enamels or lacquers. Sufficient tests of other paints and enamels have not been made to determine whether the cycle and factor used in testing flat wall paints can be applied promiscuously in the examination of miscellaneous products.

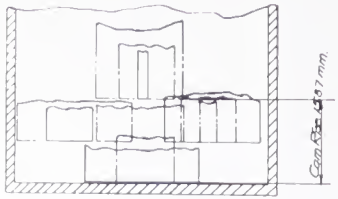
The usual means of examining and the terms used for describing the degree of settling in a paint are often indefinite and inaccurate. The use of glass jars makes it possible to accurately measure the amount of settled pigment or supernatant clear liquid and easy to detect any objectionable condition, such as a layer of gel or skin. The amount is usually not of as great importance as the condition of the settled material. The penetration tests used for asphalt, greases and paste paints, are not suitable for examining the settled material in a paint, which often varies from a soft paste in the upper portion to a hard almost dry layer at the bottom. A special penetrometer is used which consists of a vertically supported rod with a pan at the top for weights and a small plunger attached at the bottom. Three different plungers, which vary in shape and size but are of equal weight, are used. The tip of the plunger is brought in contact with the top surface of the settled material, released and the distance traveled in thirty seconds recorded. If complete penetration does not result in thirty seconds the test is repeated with



Settled Paint Mixing Machine

Centrifuge





Double Size

Diagram of Mixing Motions of Mixing Machine

Comparative Results between Natural Settling and Accelerated Settling
(Photographed 3/20/28)

Comparative Results between Natural Settling and Accelerated Settling
(Photographed 3/20/28)

the weight increased. Experience demonstrated that the movement of the plunger after thirty seconds is inappreciable and if complete penetration is not obtained in thirty seconds, additional weight is necessary, so as an expediency thirty seconds was adopted as standard. Tests are continued choosing a new spot for each test until complete penetration is obtained. By determining the load necessary to penetrate the settled cake with at least two of the plungers, a measure is obtained of the relative degree of packing. A penetrometer has been devised to automatically record the nature of the settled pigment layer throughout its depth.

In addition to the amount of supernatant liquid and the hardness of the settled cake, the work required to reincorporate the settled pigment and the possibility of obtaining a smooth product are of importance. In this laboratory this information is obtained with a special stirring apparatus. Three different mixing actions are produced with it—a rotation of the stirrer on its own axis, a rotation of the stirrer around the longitudinal axis of the glass jar and a vertical up and down motion of the stirrer. A very rapid and thorough mixing is obtained in a few minutes and even the hardest type of caked pigment can be reincorporated. The time required to produce a smooth product can be used as a measure of the work necessary.

One of the greatest objections to settling in a paint is that often when mixed by the consumer a specky product is obtained. Usually this is due to improper or insufficient mixing. When duplicate samples are available this machine affords an excellent means of determining whether a specky product would be the result of improper mixing or actually due to granulation of the paint. One of the samples is tested by first pouring off the supernatant liquid and adding it gradually during mixing, while the other is mixed direct. A specky product in both cases is definite indication of granulation in the paint.

Another property of interest is the condition of the settled pigment, that is, whether it is dispersed, flocculated, aggregated or gelled. This information can be determined by microscopical examination. Indications are that microscopical investigation of the whole subject of settling offers rich possibilities. Simple examination of the pigment in different portions of a settled paint often furnishes valuable leads as to the cause of settling and possible means of improving the product. Although a large number of settled paints have been microscopically examined in this laboratory, this subject has not been sufficiently investigated to warrant definite conclusions.

In Tables II, III and IV are results of accelerated settling of three typical flat wall paints, using a twenty-four hour cycle of heating and centrifuging. Paints "A" and "B" have fair non-settling properties and

normally would not settle to an objectionable cake within a year. Paint "C" is not as satisfactory in this respect, settling more rapidly and to a harder cake.

Table I covers tests on samples of the same paints which had settled during normal storage. They do not represent a sufficient number of different periods of aging to perhaps justify drawing definite relations between shelf storage and the accelerated cycle. Still, a comparison of the results of the Penetration Tests (ignoring the results on the sample of paint B which was tested after eight months' storage and apparently falls somewhat out of line) one finds that each twenty-four hours of the cycle represents approximately five months' shelf storage.

During the past two years this test has been used quite extensively in this laboratory in studying both the effect of the properties of pigments and variations in paint formulations on the settling tendencies of paints. The information obtained has been of appreciable value. Duplicate tests and actual shelf storage in a number of cases have shown the accelerated results to be both indicative and reliable. A large number of commercial Flat Wall Paints have been examined. Table V contains the results on six representative first grade flat wall paints.

From the results the paints would be graded for non-settling properties in the following order: A (the best), C, F, E, and B and D (the poorest). Paints A and C have excellent non-settling properties and neither should cake badly when stored from one to two years. Paint F has good non-settling and should cause no trouble unless held over a year. Paints E, B and D all have poor non-settling properties and will settle to an objectionable amount within a year. E packs slightly harder than B and D during the first few months but then slows up so that at the end of a year or two it should be in better condition than the other two. There is very little choice between B and D.

Several outside paints and enamels, that were known, from previous observations, not to develop settling even after several years of storage, were tested. No settling was obtained in any case, after seven days, when the tests were discontinued.

It is not claimed that either a perfected test or an ideal cycle has been developed, but it is believed that the results obtained definitely demonstrate that a test applying heat and centrifugal force is an excellent tool with which the settling tendencies of a paint can be determined.

TABLE I

FLAT WALL PAINTS

Shelf Aged—Examined March 20, 1928

Paint	Date Filed	Depth of Supernatant Liquid cm	Penetration Test[1] Plunger No.	Penetration Test[1] Weight Grams	Microscopic Examination of Settled Pigment
A	7/20/27	2.5	1	92	Top—Partially flocculated
	Aged 8 Mos.		2		Bottom—Partially flocculated
			3	342	
A	3/2/26	2.95	1	1042	Top—Flocculated
	Aged 2 Years		2	....	Bottom—Partially flocculated, considerable dispersed material apparently dry
			3	....	
B	7/20/27	2.6	1	242	Top—Flocculated
	Aged 8 Mos.		2	342	Bottom—Dispersed, apparently quite dry
			3	....	
B	3/2/26	2.7	1	1042	Top—Partially flocculated
	Aged 2 Years		2	....	Bottom—Dispersed
			3	....	
C	1/31/28	2.3	1	....	Top—Partially flocculated
	Aged 2 Mos.		2	42	Bottom—Partially flocculated
			3	242	
C	11/1/27	2.6	1	92	Top—Dispersed
	Aged 4½ Mos.		2	342	Bottom—Dispersed large pieces of inert pigment fairly dry
			3	....	

[1]The weight of the empty pan, rod and plunger is 42 grams, as this represents the minimum weight that can be applied, otherwise the weight given is the minimum tested, that produced complete penetration in thirty seconds. Where results are not given no tests were made.

TABLE II

Accelerated Test Using Centrifugal Force and Heat

FLAT WALL PAINT "A"

Standard Cycle[2] Hours	Depth of Supernatant Liquid Centimeters	Penetration Test[1] Plunger No.	Weight Grams	Microscopic Examination of Settled Pigment	Reincorporation Test Minutes[4]
24	1.0	1	42	Very little hard sediment at bottom.	1
		2	92	Entire mass flocculated	
		3	142		
48	2.6	1	342	Top—Flocculated	1½
		2	342	Bottom—Hard dry cake that appears aggregated	
		3	542		
72	2.6	1	342	Top—Flocculated	1½
		2	342	Bottom—Some dispersed pigment and hard aggregates	
		3	542		
96	2.6	1	742	Top—Flocculated	2
		2	1042	Bottom—Some dispersed pigment and hard aggregates	
		3	1042		
120	2.8	1	1542	Top—Flocculated	2½
		2	[illegible]	Bottom—Thick, dry layer partially flocculated and large amount of hard	
		3	[illegible]	aggregation	
144	3.1	1	1542[3]	Top—Small amount of dispersed pigment	3
		2	[illegible]	Bottom—Very dry and considerable amount of hard aggregates	(granular)

[1]See foot note[1] to Table I.

[2]*Standard 24 hr. Cycle*

Approximately 18 hours heat 65°-70°C.
Twenty minutes centrifuge at 1000 R.P.M.
Approximately 5 hours heat 65°-70°C.
Twenty minutes centrifuge at 1000 R.P.M.

[3]Incomplete penetration not tested with heavier weights.

[4]Minutes required to mix to uniform consistency.

TABLE III

Accelerated Test Using Centrifugal Force and Heat

FLAT WALL PAINT "B"

Standard Cycle[2] (Refer Table II) Hours	Depth of Supernatant Liquid Centimeters	Penetration Test[1] Plunger No.	Penetration Test[1] Weight Grams	Microscopic Examination of Settled Pigment	Reincorporation Test Minutes[4]
24	1.0	1	42	Very little hard sediment at bottom	1
		2	92	Entire mass flocculated	
		3	242		
48	1.5	1	142	Top—Flocculated	1½
		2	242	Bottom—Hard dry cake and hard aggregates	
		3	312		
72	1.7	1	542	Top—Flocculated	2
		2	542	Bottom—Thick layer of dry, lumpy material, partly dispersed	
		3	542		
96	1.9	1	742	Top—Flocculated	2½
		2	942	Bottom—Dry and lumpy material	
		3	[illegible]		
120	1.9	1	1542[3]	Top—Flocculated	3
		2	[illegible]	Bottom—Thick layer of dry material	
		3	[illegible]		
144	2.5	1	1542[3]	Top—Flocculated	3[5] (granular)
		2	[illegible]	Bottom—Very dry and lumpy	
		3	[illegible]		

[1]See foot note[1] to Table I.

[2]See foot note[2] to Table II.

[3]See foot note[3] to Table II.

[4]See foot note[4] to Table II.

[5]On duplicate sample clear liquid was poured off, material mixed two minutes and vehicle added in small portions. A smooth product was obtained in six minutes.

TABLE IV

Accelerated Test Using Centrifugal Force and Heat

FLAT WALL PAINT "C"

Standard Cycle[1] (Refer Table II) Hours and Treatment	Depth of Supernatant Liquid Centimeters	Penetration Test[2] Plunger No	Penetration Test[2] Weight Grams	Microscopic Examination of Settled Pigment	Reincorporation Test Minutes[4]
20 hours, 20 mins.					
Oven—18 hrs.		1	142	Top—Flocculated	
Centrifuge—20 mins.	1 9	2	242	Bottom—Flocculated	2
Room—2 hrs.		3	542		
24 hours, 10 mins.					
Oven—22 hrs.		1	342	Top—Flocculated	
Centrifuge—10 mins.	3 6	2	542	Bottom—Small amount of dispersed material	2½
Room—2 hrs.		3	1042		
43 hours					
Oven—40 hrs.		1	542	Top—Flocculated	
Centrifuge—60 mins.	3 7	2	542[3]	Bottom—Flocculated with some apparently dry pigment	2½
Room—2 hrs.		3	1042		
67 hours, 10 mins.					
Oven—64 hrs.		1	1042	Top—Flocculated and lumpy	
Centrifuge—100 mins.	4 0	2	1042	Bottom—Hard aggregates and dispersed pigment that	5½
Room—2 hrs.		3	....	appears dry	Formed lump which dispersed very slowly

[1]See foot note[1] to Table I.
[2]See foot note[2] to Table II.
[3]See foot note[3] to Table II.
[4]See foot note[4] to Table II.

TABLE V

Accelerated Test Using Centrifugal Force and Heat

COMMERCIAL FLAT WALL PAINTS

Standard Cycle[2] Hours	Death of Supernatant Liquid Centimeters A	B	C	D	E	F	Plunger No.	Penetration Tests[1] A Wt. Gms.	B Wt. Gms.	C Wt. Gms.	D Wt. Gms.	E Wt. Gms.	F Wt. Gms.	Reincorporation Test[3] Minutes A	B	C	D	E	F
24	0.8	1.6	2.1	1.3	0.8	1.1	1	42	142	117	62	267	92	1	1½	1½	1½	2	1½
							2	42	192	192	92	392	117						
							3	42	292	267	192	712	242						
48	2.0	3.1	3.5	3.1	1.9	2.2	1	42	512	267	592	442	217	1½	3	2	2½	2½	2
							2	92	712	367	1012	712	267						
							3	142	1012	612	....	1012	512						
72	3.0	3.5	3.7	3.7	2.6	3.0	1	92	812	367	812	192	217	2	3½	2½	3	3	2½
							2	142	1012	192	1012	1012	292						
							3	212	....	692	....	....	812						
96	3.2	3.5	3.8	1.2	3.5	3.0	1	142	1012	367	1012	1012	242	2	1½	2½	1½	3½	3
							2	192	....	492	....	1012	367						
							3	267	....	692	....	....	1012						

[1]See foot note[1] to Table I.

[2]See foot note[2] to Table II.

[3]See foot note[4] to Table II.

Assembly of Equipment used for Determination of Accelerated Settling of Paints

The World's Standard for Zinc Products